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RESEARCH ARTICLE

Kinetic processes and stable isotopes in cave dripwaters as indicators of winter severity

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Abstract

We examine how the stable isotope composition of meteoric water is transmitted through soil and epikarst to dripwaters in a cave in western Romania. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation at this site are influenced by temperature and moisture sources (Atlantic and Mediterranean), with lower $\delta^{18}\text{O}$ in winter and higher in summer. The stable isotope composition of cave dripwaters mimics this seasonal pattern of low and high $\delta^{18}\text{O}$, but the onset and end of freezing conditions in the winter season are marked by sharp transitions in the isotopic signature of cave dripwaters of approximately 1 ‰. We interpret these shifts as the result of kinetic isotopic fractionation during the transition phase from water to ice at the onset of freezing conditions and the input of meltwater to the cave at the beginning of the spring season. This process is captured in dripwaters and therefore speleothems from Urşilor Cave, which grew under such dripping points, may have the potential to record past changes in the severity of winters. Similar isotopic changes in dripwaters driven by freeze–thaw processes can affect other caves in areas with winter snow cover, and cave monitoring during such changes is essential in linking the isotopic variability in dripwaters and speleothems to surface climate.

KEYWORDS

cave, dripwaters, karst, kinetics, stable isotopes, winter climate

1 | INTRODUCTION

The stable isotopes of oxygen and hydrogen have been used for more than half of century to understand the hydrological cycle on regional and global scales (Dansgaard, 1964; Gat, 1981) as well as infer past climate changes by measuring their variability in ice cores (Oeschger et al., 1984; Thompson, Mosley-Thompson, Dansgaard, & Grootes, 1986), speleothems (Bar-Matthews, Ayalon, & Kaufman, 1997; Hendy & Wilson, 1968), ostracod shells (von Grafenstein, Erlenkeuser, Müller, Trimborn, & Alefs, 1996), or tree cellulose (McCarroll & Loader, 2004).

Since the initial recognition of speleothems as palaeoclimate archives (Hendy & Wilson, 1968), oxygen isotopes in speleothems

have increasingly been used to reconstruct changes in past climates (McDermott, 2004), providing arguably some of the highest resolution and best dated records of past climate changes (Henderson, 2006). Most of these reconstructions rely on the relationship between $\delta^{18}\text{O}$ in rainwater and local climate and the transfer of this signal into the cave environment and speleothem carbonate (Fairchild & Baker, 2012; Lachniet, 2009). Insofar as the transfer of this climate signal through the vadose zone, it is necessary to monitor the changes in the stable isotopic signature of both rain and cave waters through time, together with changes in dripwater hydrology (Harmon, 1979). Studies investigating these variables have focused on the hydrological link between dripwaters and precipitation events. They report either

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significant seasonal variability of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and a fast response to outside climate (Breitenbach et al., 2015) or significant mixing in the vadose zone with long transfer times between the surface and the cave site, and a corresponding subdued response of water isotopes in dripwaters to high-frequency changes in climate variables (Riechelmann et al., 2011). Knowledge of these response times can then be used to address specific questions related to either short- or long-term climate changes that are likely to be recorded in speleothems.

Robust interpretation of speleothem $\delta^{18}\text{O}$ requires therefore an understanding of both regional influences on rainwater isotopic signature (e.g., source and temperature) and also of the local karst processes (e.g., prior calcite precipitation, kinetic vs. equilibrium fractionation) that can modify this regional signal. The Global Network of Isotopes in Precipitation (GNIP) is a valuable resource used to investigate temporal and spatial variability of stable isotopes in precipitation, but the distribution of GNIP stations in Eastern Europe is very sparse. As a result, the interpretation of stable isotope-based climate proxies in this region is dependent on extrapolation of climate $\delta^{18}\text{O}$ (or $\delta^2\text{H}$) relationships identified in nearby regions. However, as Eastern Europe lies at the intersection of Atlantic, Mediterranean, and continental climatic influences, such extrapolations do not accurately reflect the local isotopic variability in precipitation. Consequently, climate reconstructions using $\delta^{18}\text{O}$ –climate relationships in various sedimentary archives (e.g., speleothems) have difficulties distinguishing between changes in local climate and/or shifts in climatic influences that could be interpreted as changes in climate variables. Romania has a very diverse karst landscape, offering a great potential for reconstructing past climate based on cave deposits (Constantin, Bojar, Lauritzen, & Lundberg, 2007; Drăgușin et al., 2014; Onac et al., 2015; Onac, Constantin, Lundberg, & Lauritzen, 2002; Tămaș, Onac, & Bojar, 2005). However, there are only a few studies available which documented the rainwater $\delta^{18}\text{O}$ variability and corresponding cave dripwater changes in the region (Drăgușin et al., 2017; Perșoiu, Onac, Wynn, Bojar, & Holmgren, 2011), making the climatic interpretation of speleothem $\delta^{18}\text{O}$ from this region ambiguous.

Here, we present an 11-month monitoring study that examines how the isotopic signal of meteoric water is transmitted through soil and epikarst to a cave in western Romania. We use $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from precipitation and cave dripping water in the context of karst systems and focus on the processes by which climate signals in stable isotopes are transferred from the atmosphere through the epikarst into cave

environments (Matthey et al., 2008; McDermott, Schwarcz, & Rowe, 2005). This study addresses the following goals: firstly, on a global scale, the vast majority of climate proxies are registering either summer climatic conditions (mainly biological proxies) or annual ones, with limited information existing on past winter climate changes (Perșoiu et al., 2017). Knowledge of these would greatly improve our understanding of past climate changes, as well as the ability to forecast future ones, and therefore we focus on isotopic changes in cave dripwaters that occur during the winter season. Secondly, we evaluate the degree to which the kinetic effects associated with water freezing can influence the isotopic signature of speleothems and their climatic interpretation.

2 | STUDY AREA

Urșilor (Bears) Cave ($46^{\circ}55' \text{ N}$; $22^{\circ}56' \text{ E}$) is located in the Bihor Mountains, western Romania, at 482 m above sea level (Figure 1). The cave was discovered in 1975 after blasting in a quarry mining recrystallised Upper Jurassic limestone (Rusu, 1981). The total length of the passages, extending over two levels, is 1,500 m. Before discovery, the cave had no natural entrance, but the sizable number of cave bear remains suggest these large mammals had access into the cave during the Last Glacial period. The entrance was subsequently sealed by breakdowns and secondary calcite deposits. The climate in the area is continental temperate, with an annual mean temperature of 9°C . The mean annual precipitation amount is 650 mm, with the highest values occurring in May and June and the lowest in October. Urșilor Cave is one of the main touristic caves in Romania, and it is therefore difficult to establish its natural climate conditions before the cave was developed for tourism. However, monitoring of air temperatures in the cave on three occasions (Racoviță, Moldovan & Rajka, 1998–1999; Racoviță, Onac, Feier & Menichetti, 2002–2003) and this study found changes in temperature with a maximum amplitude of $\sim 2^{\circ}\text{C}$ between colder (10°C) and warmer months (12°C), although during some milder winters the amplitude of temperature change can be as small as 0.3°C in some parts of the cave. The cave air is characterized by high relative humidity (over 95%); thus, evaporation effects in the cave are considered minimal (Racoviță, Onac, Feier & Menichetti, 2002–2003). Limestone cover above the cave increases progressively from 10 m near its entrance to around 200 m atop of the monitoring site.

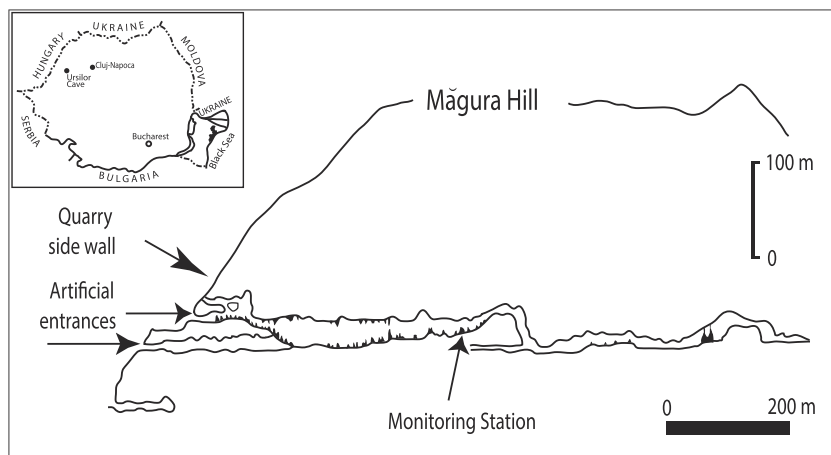


FIGURE 1 Map of Urșilor Cave with the location of the monitoring site

3 | METHODS

Samples of precipitation and cave dripwater were continuously collected between July 2010 and June 2011 and stored at 4 °C until stable isotope analysis. Near the cave, a HOBO® multichannel weather station was used to record temperature (0.02 °C resolution at 25 °C), relative humidity (0.1 % at 25 °C or ± 2.5 % from 10 % to 90 %), and precipitation amount (rain and snow; ± 0.2 mm) every hour. Precipitation samples were collected every week in 50 ml Nalgene bottles. Cave dripwater was collected using an automated 6712 Portable Teledyne sampler every 100 hr by feeding each bottle with a maximum of 900 ml of dripwater. Any excess water was automatically discarded via an overflow tube. Gemini TinyTag 2 Plus (TGP-4500) data loggers recorded temperature (± 0.01 °C) throughout the time interval of this research. To prevent evaporation of water samples collected at surface, we used a dip-in-sampler, which was buried in the soil. The device used to collect cave dripwater had dip-in-samplers (with their tubes passing through the bottle cap) locked in a water-proof container. The high relative humidity (over 98 % year around) near the sampling site makes evaporation unlikely. Determination of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for water samples was carried out on a Thermo Delta V Isotope Ratio Mass Spectrometer interfaced with a GasBench II at the University of South Florida Stable Isotope Laboratory. Results are expressed as δ values referenced to the International Vienna Standard Mean Ocean Water and values are given as per mil (‰). Analytical precision (1σ) was ± 0.8 ‰ for $\delta^2\text{H}$ and ± 0.1 ‰ for $\delta^{18}\text{O}$, respectively.

To determine the origin of the air masses delivering precipitation at our site, we used the hybrid single particle Lagrangian integrated trajectory model (HYSPLIT; Stein et al., 2015) with the gridded Global Data Assimilation System meteorological dataset (0.5° resolution). HYSPLIT has been previously used as a tool for tracking atmospheric circulation and relation with stable isotopes in precipitation (Ersek, Mix, & Clark, 2010; Sjostrom & Welker, 2009). Back trajectories were started at 500 m above ground level and run for a period of 96 hours before arrival. For each precipitation event, we chose the start time of the trajectories to correspond with the highest hourly precipitation amount for that day. A sensitivity test with trajectories started 2 hours before or after the selected time indicated no significant differences in trajectory parameters.

4 | RESULTS

4.1 | Rainwater

Stable isotope values in precipitation range from -128.4 ‰ (January) to -16.4 ‰ (August) for $\delta^2\text{H}$ and between -17.4 ‰ (January) and -1.9 ‰ (June) for $\delta^{18}\text{O}$. There is a significant correlation between the mean monthly temperature and $\delta^{18}\text{O}$ ($r = 0.816$, $P = 0.002$; Figure 2a), whereas the correlation between monthly precipitation amount and $\delta^{18}\text{O}$ is not significant ($r = 0.289$, $P = 0.388$). The stable isotope composition of rainfall and dripwater is plotted against the Global Meteoric Water Line (GMWL) and the Eastern Mediterranean Meteoric Water Line (EMMWL) is illustrated in Figure 2b. The Local

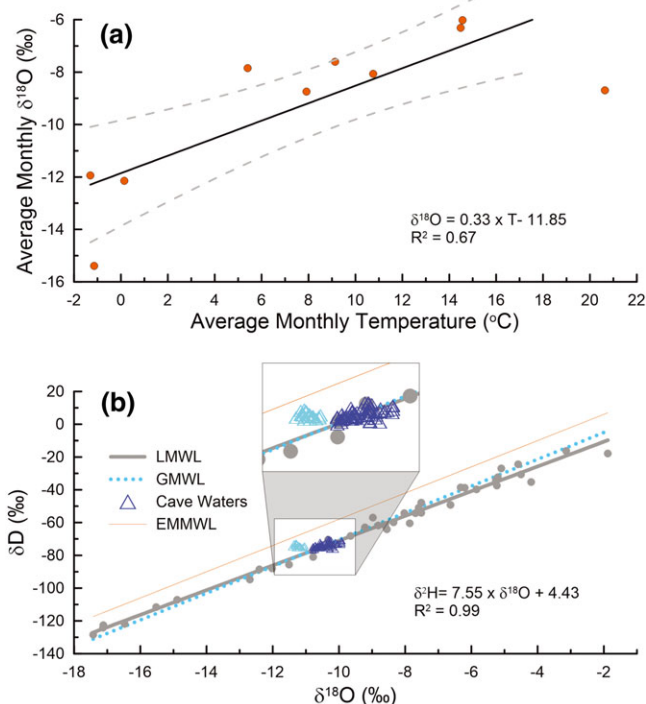


FIGURE 2 (a) Average monthly air temperature plotted against monthly rainwater $\delta^{18}\text{O}$ for the period 2010–2011 at Urşilor Cave. Dashed grey lines indicate the confidence interval of the regression, (b) the Local Meteoric Water Line (LMWL) at Urşilor Cave compared with the Global Meteoric Water Line and the Eastern Mediterranean Meteoric Water Line. Grey circles indicate the stable isotope composition of rainwater and the dark blue triangles show the stable isotope values of dripwaters. Cyan triangles indicate the isotopic values of dripwaters affected by freezing conditions

Meteoric Water Line (LMWL) is $\delta^2\text{H} = 7.55 \times \delta^{18}\text{O} + 4.43$, with average $\delta^{18}\text{O}$ of -9 ‰ (± 4.03 , 1σ) and average $\delta^2\text{H}$ of -63 ‰ (± 30.6 , 1σ).

4.2 | Dripwaters

The average cave dripwater $\delta^2\text{H}$ is -73.9 ‰ (± 1.5 , 1σ) and the average $\delta^{18}\text{O}$ is -10.6 ‰ (± 0.4 , 1σ). The dripwaters have a much reduced amplitude compared with rainwaters ($\delta^2\text{H}$ amplitude is 6.9 ‰ whereas the $\delta^{18}\text{O}$ amplitude is 1.5 ‰). They plot largely on the LMWL (Figure 2), but there is a distinct group of samples with values between the EMMWL and LMWL. Starting in early December, a sharp drop of ~ 1 ‰ in the $\delta^{18}\text{O}$ values (and $\delta^2\text{H}$) occurs (Figure 3a), followed by relatively constant values (± 0.1 ‰) until early March when there is a similarly abrupt $\delta^{18}\text{O}$ rise of ~ 1 ‰. These sharp transitions are also seen in the d-excess values of the dripwater (Figure 3b). Although $\delta^{18}\text{O}$ in precipitation during winter is generally lower than in the rest of the year, the transition to more negative values is not as abrupt as in dripwaters, suggesting that processes occurring during water percolation through soil and epikarst modify the isotopic signature of rainwaters.

4.3 | Precipitation Trajectories

The HYSPLIT back trajectories indicate a predominantly North Atlantic origin for air masses reaching Urşilor Cave, as expected from

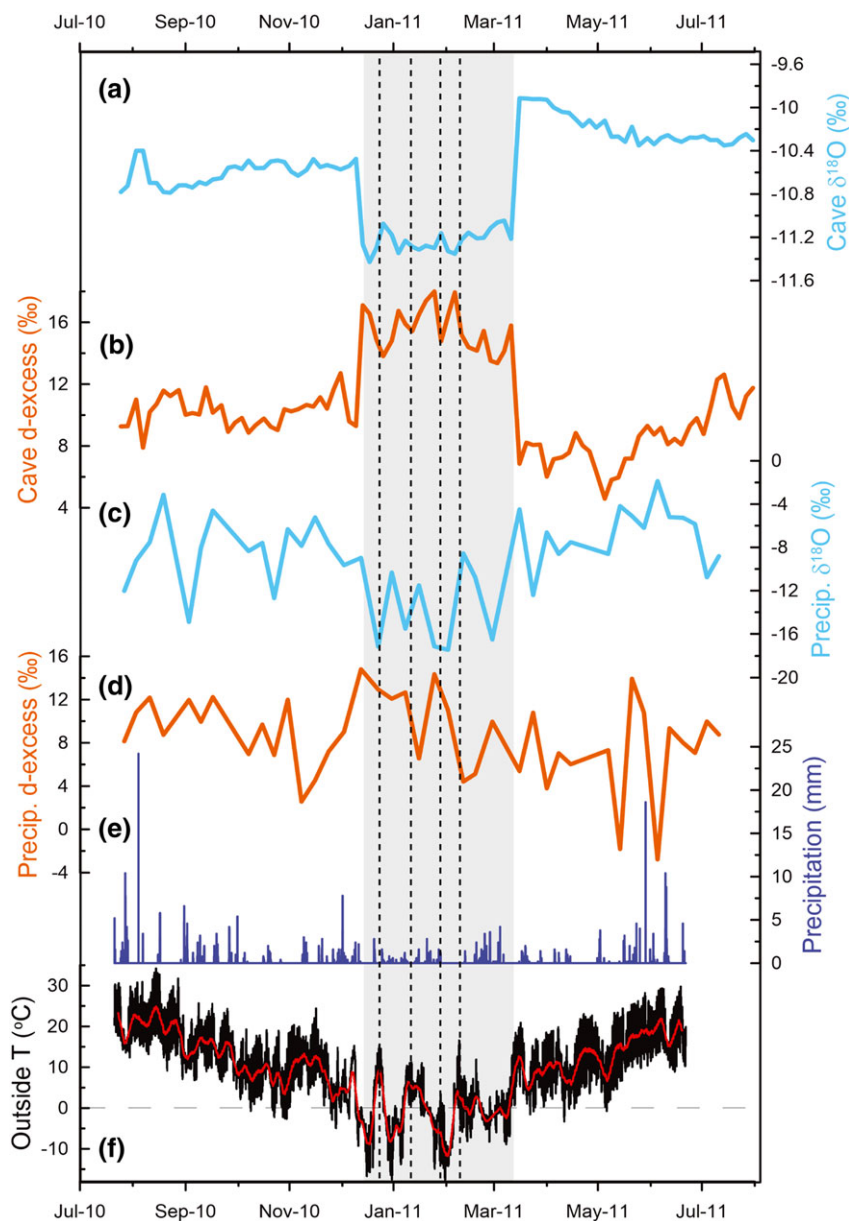


FIGURE 3 Local temperature and precipitation amount at Urșilor Cave compared with the stable isotopic values of rain and dripwaters. (a) $\delta^{18}\text{O}$ values in dripwaters, (b) deuterium excess in dripwaters, (c) precipitation $\delta^{18}\text{O}$, (d) deuterium excess in precipitation, (e) precipitation amount, (f) temperature outside the cave recorded hourly (black line) and the daily average (red line). Grey bar shows the period with low $\delta^{18}\text{O}$ values in cave dripwaters and dashed vertical lines mark exterior temperature maxima after periods of freezing conditions in winter. Dashed horizontal line in panel f marks the 0°C temperature

the general atmospheric circulation in the region. Looking at the events which delivered rainwater with isotopic values below or above the average ($\pm 1\sigma$) it is apparent that samples with the lowest $\delta^{18}\text{O}$ values have largely a North Atlantic origin and/or have a longer atmospheric transport pathway than samples with high $\delta^{18}\text{O}$ values (Figure 4). In contrast, storms characterized by higher than average $\delta^{18}\text{O}$ values have a more proximal or Mediterranean origin.

5 | DISCUSSION

5.1 | Stable isotopes in precipitation

The seasonality of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation is reflective of the temperature influence of the stable isotope composition of rainwater (Figures 2a and 3). The annual cycle of stable isotope values in precipitation is mirrored by similar variability in deuterium excess (d-excess) ($d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$; Dansgaard, 1964) with low values in summer and

high in winter (Figure 3). The low d-excess values in summer precipitation are likely reflecting secondary evaporative effects of the falling rain drops through dry atmosphere (Gat & Carmi, 1970), whereas the higher autumn and winter values could be indicative of moisture sourced in the Eastern Mediterranean (Vreča, Bronić, Horvatinčić, & Barešić, 2006) as well as of those that underwent local recycling and/or originating from eastern trajectories (Figure 4).

The average values of $\delta^2\text{H}$ (-63‰) and $\delta^{18}\text{O}$ (-9‰) in precipitation are slightly lower than those in SW Romania (-60.5‰ and -8.8‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively, at Dumbrava [Bojar, Halas, Bojar, & Chmiel, 2017] and -53‰ and -8.3‰ , respectively, at Drobeta Turnu-Severin [Drăgușin et al., 2017]) but higher than those in the central Bihor Mountains at Scărișoara (-88‰ and -12‰) and the Hațeg Basin (-76‰ and -10.8‰ ; Bojar, Ottner, Bojar, Grigorescu, & Perșoiu, 2009). However, in SW Romania, a higher proportion of precipitation is sourced from the Mediterranean Sea, and mean annual air temperatures are higher by approximately 0.5°C than at Urșilor Cave, thus accounting for the higher stable isotope values in

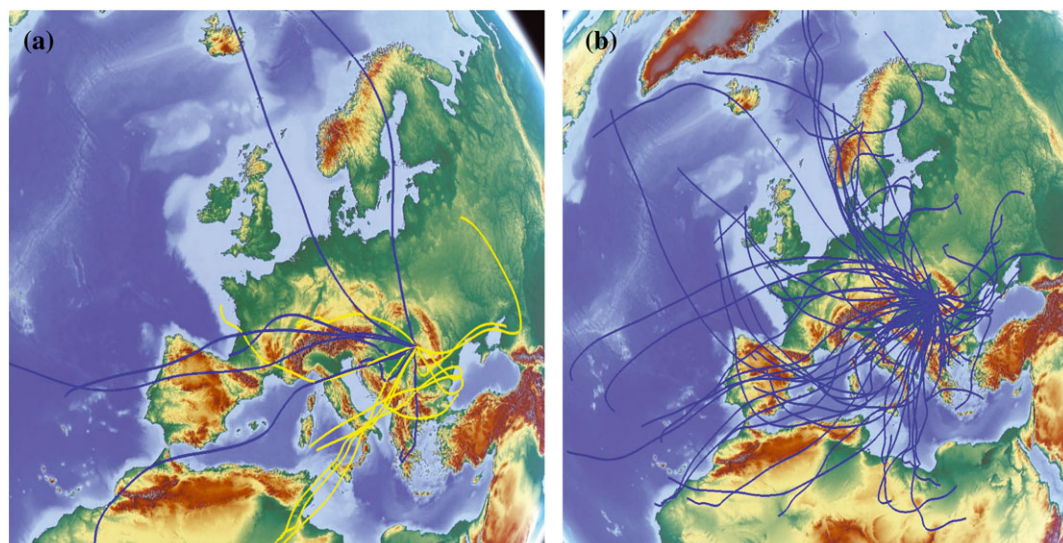


FIGURE 4 (a) Map showing the HYSPLIT-based trajectories of airmasses delivering ^{18}O -depleted (blue) and ^{18}O -enriched (yellow) rainwaters at Urşilor Cave ($\pm 1\sigma$), (b) HYSPLIT trajectories for all precipitation events recorded at Urşilor Cave, except those from panel a

precipitation there. Moreover, Scărișoara and Hațeg are located further inland and at higher altitudes than the Urşilor site, thus possibly accounting for the lower stable isotope values. Taken together, these data suggest that temperature effects, moisture sources, and rainout effects combine to determine the stable isotope composition of precipitation in the region, with Urşilor site receiving more Atlantic-sourced moisture than SW and central Romania. However, d-excess values and the HYSPLIT-modelled trajectories suggests that at least during late autumn and winter, Mediterranean cyclones penetrate northward, bringing moisture enriched in the heavy isotopologues of water to the Urşilor cave site. These precipitation events, however, are less important in terms of quantities of water delivered to the site (Figure 3), thus leaving the Atlantic Ocean as the main source of water feeding the drip sites in the cave.

5.2 | Effect of freezing on stable isotopes in dripwaters

The stable isotope composition of the dripwater shows a similar trend to that in precipitation, with two intervals of higher values in summer–autumn 2010 and spring–summer 2011, separated by a period of lower values (winter 2010–2011). However, contrary to the relatively smooth and continuous transition from high to low values and vice versa seen in the precipitation isotopic values, the similar changes in the dripwater isotopic record are abrupt, marked by a shift of about 1‰ in $\delta^{18}\text{O}$ (Figure 3c). This shift is mirrored by a similar one for the d-excess values, which increase abruptly in December (by $\sim 8\%$) and decrease, with the same magnitude, in March (Figure 3b). These abrupt shifts in the d-excess record are not seen in the precipitation d-excess, which has rather jagged variations throughout the entire record.

The abrupt change towards low $\delta^{18}\text{O}$ (and high d-excess) in dripwater occurs at the onset of freezing outside the cave and the similarly sudden shift towards high $\delta^{18}\text{O}$ (and low d-excess) values is synchronous with the increase of external temperatures above 0°C . The occurrence of freezing conditions outside the cave during

intervals with low $\delta^{18}\text{O}$ in dripwater suggests that the following mechanism may explain the extreme variability of the isotopic values in dripwater. Freezing of water results in strong fractionation due to the temperature difference at which the various water isotopologues freeze (Souchez, Petit, Tison, Jouzel, & Verbeke, 2000). As a result of this process, the heavy (^{18}O and ^2H) isotopes in the water will be preferentially incorporated in the ice (Jouzel & Souchez, 1982; Perşoiu et al., 2011), leaving the remaining water available to reach the cave relatively (to the ice) depleted in these isotopic species. This “freezing signal” is further carried to the cave and recorded by the abrupt drop in dripwater $\delta^{18}\text{O}$ and similarly rapid increase in d-excess. As isotopic fractionation occurs under both equilibrium (at very low freezing rates) and kinetic conditions during the freezing of water (Souchez et al., 2000), the resulting variable fractionation factors led to the alignment of the ice along a line (in a $\delta^{18}\text{O}$ – $\delta^2\text{H}$ diagram) with a slope lower than 8 (a so-called “freezing slope”; Jouzel & Souchez, 1982). This, in turn, results in the d-excess of the ice and remaining water having higher values than those in the parent water, as seen in our data: d-excess in precipitation (parent water) has a mean value of 9‰ and the associated dripwater a value of about 10‰ before freezing, whereas during the interval with negative air temperatures, the d-excess in dripwater (reflecting that of the remaining water after some of the parent one was incorporated in ice at the surface) increase abruptly to 15.5‰. At the onset of melting, release of the water from the ^{18}O (and ^2H)-enriched ice is seen in the isotopic values of the dripwater as a rapid increase in $\delta^{18}\text{O}$ and associated sudden drop in d-excess values (Figure 3a,b). Similar processes occurred during brief periods of warming during the winter that resulted in melting of the ice at the surface and the release of ^{18}O -enriched water that reached the cave, as seen in Figure 3, which shows a one-to-one coupling between positive external temperatures, peaks in the $\delta^{18}\text{O}$, and troughs in the d-excess dripwater records.

We have observed ice formation by water freezing on the ground, during the monitoring period. The enrichment of ice in the heavy isotopes (^2H and ^{18}O) during freezing of water was documented by

numerous authors, both experimentally (O'Neil, 1968) and in the field (Árnason, 1969; Jouzel & Souchez, 1982; Perşoiu et al., 2011; Souchez & Jouzel, 1984).

Continuous dripping in winter (and partial freezing of precipitation water at the surface) empties the storage zone above the cave. The preferential incorporation of heavy isotopes of H and O in the ice at the surface renders the remaining water progressively depleted in heavy isotopes. The onset of melting in spring sends a pulse of ^2H (and ^{18}O)-enriched water (Figure 3) that mixes with this stored one and then is slowly released in cave as dripwater. Higher and less variable d-excess values in dripwaters compared with those in precipitation are also indicating that water resulting from ice melting is the main contributor to the recharge of the dripping site.

Freezing at the surface results in low amounts of water available for infiltration and continuous dripping in the cave shows that the cap rock slowly but constantly dries out, as such leaving little water in the matrix available for mixing once surface melting leads to renewed infiltration. Thus, according to a simple mass and isotope balance, this limited amount of water, depleted in heavy isotopes has a reduced influence of the stable isotope composition of new water. Further, this ^{18}O (and ^2H)-enriched water released after melting, fills the voids in the rock above the drip site, and it slowly released as dripwater. The processes continue until the system is "purged" by the major rain event of 2011.

5.3 | Implication for paleoclimatic interpretation of $\delta^{18}\text{O}$ in speleothems

The correlation of local temperature with $\delta^{18}\text{O}$ in precipitation has a slope of $0.33\text{‰}/^\circ\text{C}$ (Figure 2a). Assuming this signal is preserved during water transport to the cave, the water–calcite $\delta^{18}\text{O}$ fractionation ($-0.2\text{‰}/^\circ\text{C}$; Tremaine, Froelich, & Wang, 2011) largely removes the influence of outside precipitation temperature on $\delta^{18}\text{O}$ in dripwaters, resulting in a net effect of $0.13\text{‰}/^\circ\text{C}$. However, the freeze–thaw processes outlined above are directly influenced by the outside temperatures and induce $\delta^{18}\text{O}$ changes of 1‰ or more in cave dripwaters. The average $\delta^{18}\text{O}$ of dripwaters in the summer months is -10.6‰ and in the winter is -11.2‰ . Based on these $\delta^{18}\text{O}$ values of dripwaters, the water–calcite $\delta^{18}\text{O}$ fractionation at cave temperatures (Tremaine et al., 2011) for the coldest (10°C) and the warmest months (12°C), we calculate a hypothetical $\delta^{18}\text{O}$ value for modern speleothem calcite deposited under equilibrium conditions in Urşilor Cave of -8.5‰ in the summer and -8.7‰ in the winter. A similar difference of 0.2‰ is also obtained if the water–calcite fractionation equation of Kim and Oneil (1997) is used (-9.54‰ and -9.73‰ for summer and winter, respectively). We therefore hypothesize that the $\delta^{18}\text{O}$ of speleothems in Urşilor Cave can be influenced by the extent of the freezing conditions during the winter season. However, this mechanism can only be valid if the dripwaters feeding the speleothems have a short residence time in the bedrock and there is limited water mixing. The rapid transfer of freezing and melting signal above the cave (as seen by the one-to-one coupling of temperatures, $\delta^{18}\text{O}$ values, and d-excess in dripwaters) implies that the aforementioned transfer is indeed quick with limited mixing during transfer. Flow along secondary porosity (fissures/cracks) as opposed to primary porosity could explain this process (Ford & Williams, 2007; Moldovan, Meleg, & Perşoiu, 2012).

6 | CONCLUSIONS

Precipitation data at Urşilor Cave in western Romania indicate a statistically significant relationship between temperature and rainwater $\delta^{18}\text{O}$, with generally lower $\delta^{18}\text{O}$ values in the winter and higher $\delta^{18}\text{O}$ values in the summer. In addition, Mediterranean cyclones that reach western Romania are generally characterized by higher $\delta^{18}\text{O}$ values in precipitation. We show that if the transit time of water is short, these influences on $\delta^{18}\text{O}$ values of cave dripwaters can be masked by isotopic fractionation during freeze–thaw processes. As a result, the $\delta^{18}\text{O}$ values of cave dripwaters at Urşilor Cave are controlled in part by the extent of the freezing conditions during winter. Therefore, speleothems from this cave have the potential to record changes in severity of winters through time, if they are fed by drips with short residence times. This process is likely to be important for determining the stable isotope composition of dripwaters in other caves from regions with seasonal snow cover which have a short water residence time and reduced mixing.

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